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AIR RESOURCES BOARD

PROCEDURE FOR THE DETERMINATION OF ETHERS AND
ALCOHOLS IN GASOLINE BY GAS CHROMATOGRAPHY

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Southern Laboratory Branch
Monitoring and Laboratory Division
State of California

Haagen-Smit Laboratory
9528 Telstar Avenue
El Monte, CA 91731

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CALIFORNIA AIR RESOURCES BOARD
MONITORING AND LABORATORY DIVISION

Procedure for the Determination of Ethers and Alcohols in Gasoline
by Gas Chromatography

1 INTRODUCTION

- 1.1 The Air Resources Board uses this SOP to determine compliance with the ethanol exclusion for Reid Vapor Pressure regulation and the ether and alcohol levels for compliance with the Wintertime Oxygenate regulation. As of March 1996 this SOP is used for determination of compliance with the Cleaner Burning Gasoline oxygenate regulation.
- 1.2 This document describes an automated method of analyzing C1 to C4 alcohols, tertiary amyl alcohol, and four ethers in gasoline by gas chromatography.
- 1.3 This method provides a procedure for the analysis of methanol (MeOH), ethanol (EtOH), isopropanol (iPA), n-propanol (nPA), isobutanol (iBA), sec-butanol (sBA), tertiary-amyl alcohol (tAA or tertiary pentanol), tertiary-butanol (tBA), and n-butanol (nBA) in gasoline in the range of 0.1 to 12.0 mass %.
- 1.4 Methyl tertiary-butyl ether (MTBE), ethyl tertiary-butyl ether (ETBE), tertiary-amyl methyl ether (TAME), and diisopropyl ether (DIPE) in gasoline are determined from 0.1 to 20.0 mass %.
- 1.5 This method is based on ASTM D 4815-94.

2 SUMMARY OF PROCEDURE

- 2.1 Gasoline samples are collected and brought to the laboratory. An internal standard, 1,2-dimethoxyethane (ethylene glycol dimethyl ether), is added gravimetrically to the samples prior to analysis. The internal standard weight is used to calculate the mass percent of each oxygenate as compared to the response for internal standard and the same oxygenate in the calibration standard. One purpose of the internal standard is providing correction for variation in injection volume.
- 2.2 Samples are injected by auto sampler into a gas chromatograph (GC) equipped with a polar pre-column, non-polar analytical column, column switching valve, and flame ionization detector (FID). The pre-column retains

the oxygenated and heavier hydrocarbons, while allowing the faster eluting light hydrocarbons to vent. The pre-column is then back flushed onto the analytical column, which separates the individual C1 to C4 alcohols, ethers, and tert-pentanol from the remaining heavier hydrocarbons. These heavy compounds are then back flushed from the analytical column upon elution of the last oxygenate of interest.

- 2.3 The data system identifies the oxygenate associated with each chromatographic peak. Oxygenate concentrations are determined by integrating and comparing the areas of sample peaks and calibration standard peaks, with reference to the internal standard.

3 MEASUREMENT INTERFERENCES AND LIMITATIONS

- 3.1 The known interference or limitation to this procedure is hydrocarbon contamination. If the valve back flush time is not set correctly, hydrocarbon peaks may co-elute with the oxygenates. This can be detected and avoided by setting the back flush time according to ASTM D 4815-94 and analyzing an unoxygenated gasoline blank daily to check for any hydrocarbon peaks.

4 EQUIPMENT, APPARATUS, REAGENTS, AND FORMS

- 4.1 Gas chromatograph, Varian model 3400 or equivalent, equipped with FID, 1,2,3-tris-2-cyanoethoxypropane (TCEP) or equivalent pre-column and DB-1 (J & W) or equivalent analytical column, connected by a 10-port valve.
- 4.2 Liquid autosampler, Varian model 8200 or 8400.
- 4.3 Digital Data Acquisition System, Varian Star or equivalent.
- 4.4 Methanol, isopropanol, n-propanol, isobutanol, sec-butanol, tert-butanol, n-butanol, and tert-pentanol, (known purity and free of other components to be analyzed), Fisher or equivalent.
- 4.5 Ethanol (absolute) Fisher or equivalent.
- 4.6 MTBE (99.8%) Aldrich or equivalent.
- 4.7 ETBE (99%) Aldrich or equivalent.
- 4.8 TAME (94%) Aldrich or equivalent.

- 4.9 Indolene or stock gasoline (without oxygenates), obtained from refineries, terminals, or commercial service stations.
- 4.10 A control standard, of typical sample concentration, is prepared as described in 7.2.
- 4.11 Gas requirements:
 - 4.11.1 Air, "Zero" grade.
 - 4.11.2 Nitrogen, 99.998%.
 - 4.11.3 Helium, 99.995%.
 - 4.11.4 Hydrogen, 99.995%.
- 4.12 The forms needed are the instrument notebook, spreadsheets for reporting results, and spreadsheets for quality control reports.

5 PROCEDURE

- 5.1 A 5 or 10 ml volumetric flask is weighed on an analytical balance. 250 uL (for 5mL) or 500 uL (for 10 mL) of internal standard (DME) is pipetted into the flask and it is weighed again. A gasoline sample is added in sufficient quantity to bring the solution to volume. The total mass is obtained.
- 5.2 Step 5.1 is repeated for each sample.
- 5.3 Each gasoline/internal standard mixture is transferred into an auto sampler vial.
- 5.4 A 2.0 uL aliquot of each sample is injected via an auto sampler into a GC configured as follows:
 - 5.4.1 Columns: Pre-column--TCEP, 20% (m/m) on 80/100 Chromosorb P(AW), stainless steel, 560 mm x 1.6 mm OD.
Analytical--DB-1, 30 m x 0.53 mm ID, 3.0 micron film thickness
Carrier gas: Helium--pre-column at 5 mL/min
analytical at 3 mL/min

Make up gas: Nitrogen at 18 mL/min,
Hydrogen at 30 mL/min and air at 300 mL/min
Detectors: FID, 250 C
Injector: 200 C, split/splitless with split ratio 15:1
Column Temp.: 60 C (isothermal)
Data system: Varian Star data station
Back flush time: 0.20 min, or the time necessary to vent light hydrocarbons,
without losing the oxygenates of interest
Reset time: 8.0 min, or any time after TAME has eluted

- 5.5 Column and split vent flows are adjusted previous to a multi point calibration, and then are checked weekly and reset as necessary.
- 5.6 One control standard and one stock gasoline blank are analyzed daily at the beginning of each set of samples.
- 5.7 The control standard is repeated every ten samples and again at the end of the run.
- 5.8 A replicate analysis is performed daily.
- 5.9 Peak identifications provided by the data system are checked and corrected, if necessary. Any misplaced baseline segments are corrected in the reconstructed chromatogram.
- 5.10 The level of peak rejection is set below the lowest peak area equivalent to 0.1 mass percent as per 1.3 and 1.4.

6 SAFETY PRECAUTIONS

- 6.1 Standard laboratory safety procedures and equipment should be used in performing this method. For example, safety glasses and gloves should be worn. All standard and sample preparation should be done in the fume hood. Gasoline contains compounds known to be toxic and carcinogenic. The internal standard, 1,2 dimethoxyethane (DME), is a known teratogen.

7 CALIBRATION

- 7.1 Calibration standards which are National Institute of Standards and Technology (NIST) traceable by weight are purchased annually or as needed and stored below 5 degrees C. The five level calibration for each oxygenate of interest is performed annually or as needed due to instrument

maintenance, and must be repeated if the linearity or intercept test fail to meet the specification of ASTM D4815-94.

7.2 If purchased standards are not available, multi-component calibration standards are prepared by mass using the appropriate amounts of individual oxygenates with Indolene or stock gasoline sufficient to bring the solution up to final mass and volume. Internal standard is added to each standard at the same concentration as it is added to samples. Each component is weighed and the mass percent of each component is calculated. For each oxygenate, prepare a minimum of five calibration standards spanning the range of the oxygenate in the samples.

7.2.1 The total mass percent of oxygenated compounds (including internal standard) of any standard must not exceed 30 mass %. These standards last up to one year if refrigerated below 5 degrees C.

8 CALCULATION OF RESULTS

8.1 Calibration and Control Standard Concentrations

The concentration of each oxygenate in the calibration and control standard is determined by the following equation.

$$\text{Concentration (Mass \%)} = \frac{\text{Mass of Oxygenate}}{\text{Total Mass}} \times 100$$

Establish the calibration curve for each oxygenate. Plot the response ratio:

$$\text{rsp}_i = (A_i / A_s)$$

where:

A_i = area of oxygenate, and
 A_s = area of internal standard

as the y-axis versus the amount ratio (amt_i) = (W_i/W_s) where

W_i = mass of the oxygenate, and
 W_s = mass of the internal standard.

as the x-axis calibration curves for each oxygenate. Check the correlation r squared value for each oxygenate. The r^2 value should be at least 0.99 or better. R^2 is calculated as follows:

$$R^2 = \frac{(\sum xy)^2}{(\sum x^2)(\sum y^2)}$$

where:

$$x = X_i - x_a, \text{ and} \\ y = Y_i - y_a$$

and

X_i = amt_{*i*} ratio data point,
 x_a = average values for all (amt_{*i*}) data points,
 Y_i = corresponding rsp_{*i*} ratio data point, and
 y_a = average values for all (rsp_{*i*}) data points.

For each oxygenate, *i*, calibration data set, obtain the linear least-squares fit equation in the form:

$$(rsp_i) = (m_i)(amt_i) + b_i$$

where:

(rsp_{*i*}) = response ratio for oxygenate *i* (y-axis),
 m_i = slope of linear equation for oxygenate *i*,
amt_{*i*} = amount ratio for oxygenate *i* (x-axis), and
 b_i = y-axis intercept.

The values of m_i and b_i are calculated as follows:

$$m_i = \sum xy / \sum x^2, \text{ and} \\ b_i = y_a - m_i x_a$$

For an optimum calibration, the absolute value of the y-intercept b_i must be at a minimum. The equation to determine the mass percent reduces to the following. The y-intercept can be tested using the same equation.

$$w_i = (b_i/m_i)(W_s/W_g)100\%$$

where :

w_i = mass % oxygenate *i*, where w_i is <0.1 mass %,
 W_s = mass of internal standard added to the gasoline sample, and
 W_g = weight of gasoline sample.

8.2 Sample Concentrations

The concentration of each oxygenate in a sample is determined by the following equation:

$$rsp_i = (m_i)(amt_i) + b_i$$

where:

rsp_i = response ratio for oxygenate i (y-axis),
 m_i = slope of the linear fit,
 b_i = y-intercept, and
 amt_i = amount ratio for oxygenate i (x-axis)

or

$$amt_i = W_i = [(rsp_i) - b_i] / m_i.$$

To obtain mass percent (w_i) results for each oxygenate

$$w_i = (W_i 100\%) / W_g$$

where:

W_i = mass of each oxygenate i .
 W_g = weight of the gasoline sample.

Volumetric concentrations of oxygenate in a sample, if desired can be calculated using the following equation:

$$V_i = w_i (D_f / D_i)$$

where:

w_i = mass percent of each oxygenate as determined in the equation above.
 V_i = volume percent of each oxygenate to be determined.
 D_i = relative density at 15.56 C (60 F) of the individual oxygenate as found in Table 1.
 D_f = relative density of the fuel under study as determined by ASTM Test Method D 1298 or D 4052.

8.3 Determination of Total Oxygen

- 8.3.1 The sum of the mass % oxygen of the individual oxygenates constitutes the total mass % oxygen in the sample.

$$\text{Oxygen Total} = \text{Oxygenate}_1 + \text{Oxygenate}_2 + \dots + \text{Oxygenate}_n$$

where:

Oxygen Total = total mass % oxygen in the fuel, and
Oxygenate i = concentration of each oxygenate (mass % oxygen)

- 8.3.2 Alternatively, total oxygen may be determined directly from the individual oxygenate concentrations, in mass %, as follows:

$$\text{OX}_{TOT} = \text{C OX}_1 \times 16.0 \times \text{N}_1/\text{M}_1 + \text{C OX}_2 \times 16.0 \times \text{N}_2/\text{M}_2 + \dots$$

where:

OX_{TOT} = total mass % oxygen in the fuel,
 C OX_i = concentration of each oxygenate (mass %),
Atomic weight of oxygen = 16.0,
 N_i = number of oxygen atoms in the oxygenate molecule, and
 M_i = molecular weight of the oxygenate.

9 QUALITY CONTROL AND ASSURANCE

9.1 Blank Analysis

A stock gasoline blank free of oxygenate is analyzed daily to check the analytical system for contamination. If the blank chromatogram shows a peak greater than 0.1 mass percent (as specified in 1.3 and 1.4) in the region of interest, the blank is repeated. If necessary, the back flush time is readjusted according to ASTM D 4815-94. All oxygenate concentrations must be below 0.1 mass percent before the analysis may proceed.

9.2 Calibration Standard Analysis

Calibration standards are purchased (NIST traceable by weight) or prepared yearly and stored below 5 degrees C. The five level calibration for each oxygenate of interest is performed yearly or as needed due to instrument maintenance, and must be repeated if the linearity or intercept tests fail the specification of ASTM D 4815-94.

9.2.1 Standard Reference Material

A NIST Standard Reference Material (SRM) containing oxygenates at a concentration simulating Cleaner Burning Gasoline is analyzed each quarter. If the determined concentration is not within plus or minus 0.46 mass percent for MTBE, the instrument and situation are examined to find the problem and the SRM is reanalyzed. If the SRM value is still not within plus or minus 0.46 mass percent for MTBE, the multiple point calibration is performed again and the SRM reanalyzed.

9.3 Control Standard Analysis

Since daily calibration is not required, a control standard is analyzed every day to monitor changes or potential problems with the calibration or instrument. The control standard is prepared in the lab and consists of target oxygenates (for example ethanol, MTBE, and TAME) at target levels simulating Cleaner Burning Gasoline. It is analyzed at the beginning of the day, every ten samples, and again at the end of the run. Whenever the control standard values differ from their predetermined or average value by more than twice the percent relative repeatability for a compound of interest, the standard must be reanalyzed. The percent relative repeatabilities are shown in Table 2 and 4.

9.4 Quality Control Charts

A multi point calibration plot is maintained for each oxygenate of interest and updated each time a multi point is performed. These are also used for the sample calculations. Quality Control (Q.C.) charts are maintained for both the control and NTRM standards and are updated weekly. These charts reflect the percent difference from the predetermined or average value.

- 9.4.1 Instrument response (area counts) to the control and NTRM standards are monitored each time analyzed to check the stability of both the instrument and the standard. Should the response change in a significant or unexplained way, the flow rates and split ratio should be checked and a new multi point run if necessary.

9.5 Replicate Analysis

A replicate analysis is performed daily and on violations. Enforcement Division staff determines violations.

- 9.5.1 For replicate samples that vary by more than the percent repeatability for each oxygenate of interest, the sample is analyzed a third time. If the closest two of the three analyses still show a difference greater than this, all samples run that day must be reanalyzed.

$$\% \text{ Difference} = \frac{\text{Difference (mass \%)}}{\text{Average (ppm)}} * 100$$

9.6 Violations

- 9.6.1 When a violation of Cleaner Burning Gasoline or the wintertime oxygenates regulations occurs, a replicate analysis of that sample should be performed. Results of the two analyses must not vary more than the percent relative repeatability for each oxygenate; and the average oxygen content of the two analyses must be below the minimum required amount or above the maximum required amount to be considered in violation.

9.7 Limits of Detection

The limits of detection (LOD) are determined annually from multi point calibration data. For each oxygenate, the three standards lowest in concentration are used to determine a linear regression. The results of this regression are used in the following equation:

$$\text{LOD} = (|b| + 3s)/m$$

where:

b = intercept

m = slope

s = standard deviation of three repeat runs of each concentration level

The LODs must be below 0.1 mass percent as specified in 1.3 and 1.4.

9.8 Repeatability and Reproducibility

See Table 2 and 3.

9.9 Documentation

A laboratory notebook is maintained by the chemist(s) and must be updated on a daily basis. Area counts and concentrations of all standards and

samples analyzed, the time of analysis, and the data file number are recorded. At the end of each day, the percent difference for control standards and replicate samples are calculated and recorded in the notebook. Column flows are also recorded weekly along with any comments regarding that day's analysis. Any maintenance performed on the instrument must also be recorded. This notebook remains on the mobile laboratory.

9.10 Quality control of the sampling procedure is overseen by Enforcement Division.

10 References

10.1 ASTM D 4815-94, "Standard Test Method for Determination of C1 to C4 Alcohols and MTBE in Gasoline by Gas Chromatography," Annual Book of ASTM Standards, Vol. 05.03.

11 Revision History

Revision No. 6 Effective Date: 11/04/96 Approval Date: 12/27/96

Revision No. 7 Effective Date: 04/01/00

Significant changes: 5.1 - Allow use of 10 ml. Volumetric Flasks

9.2.1 - Change SRM 2294 Control limits

9.6. 1 - Update Violation duplicates

Revision No. 8 Effective Date: 01/01/03

Table 1. Densities of Oxygenates

<u>COMPOUND</u>	<u>DENSITY (g/mL at 15.56 C)</u>
Methanol	0.7963
Ethanol	0.7939
Isopropanol	0.7899
t-Butanol	0.7922
n-Propanol	0.8080
MTBE	0.7460
sec-Butanol	0.8114
DIPE	0.7300
Isobutanol	0.8058
ETBE	0.7452
t-Pentanol	0.8170
n-Butanol	0.8137
TAME	0.7758

Table 2. Repeatability Estimates of Oxygenates in Gasoline
from ASTM D4815-94.

<u>Component</u>	<u>Repeatability</u>
Methanol (MeOH)	0.09 ($X^{0.59}$)
Ethanol (EtOH)	0.06 ($X^{0.61}$)
Isopropanol (iPA)	0.04 ($X^{0.56}$)
tert-Butanol (tBA)	0.04 ($X^{0.56}$)
n-Propanol (nPA)	0.003 ($X^{0.57}$)
MTBE	0.05 ($X^{0.56}$)
sec-Butanol (sBA)	0.003 ($X^{0.61}$)
DIPE	0.08 ($X^{0.56}$)
Isobutanol	0.08 ($X^{0.56}$)
ETBE	0.05 ($X^{0.82}$)
tert-Pentanol (tAA)	0.04 ($X^{0.61}$)
n-Butanol (nBA)	0.06 ($X^{0.61}$)
TAME	0.05 ($X^{0.70}$)
Total Oxygen	0.02 ($X^{1.26}$)

Table 3. Reproducibility Estimates of Oxygenates in Gasoline
from ASTM D4815-94.

<u>Component</u>	<u>Reproducibility</u>
Methanol (MeOH)	0.37 ($X^{0.61}$)
Ethanol (EtOH)	0.23 ($X^{0.57}$)
Isopropanol (iPA)	0.42 ($X^{0.67}$)
tert-Butanol (tBA)	0.19 ($X^{0.67}$)
n-Propanol (nPA)	0.11 ($X^{0.57}$)
MTBE	0.12 ($X^{0.67}$)
sec-Butanol (sBA)	0.44 ($X^{0.67}$)
DIPE	0.42 ($X^{0.67}$)
Isobutanol	0.42 ($X^{0.67}$)
ETBE	0.36 ($X^{0.76}$)
tert-Pentanol (tAA)	0.15 ($X^{0.57}$)
n-Butanol (nBA)	0.22 ($X^{0.57}$)
TAME	0.31 ($X^{0.51}$)
Total Oxygen	0.09 ($X^{1.27}$)